



Increasing silicon concentrations in Bohemian Forest lakes

J. Veselý, V. Majer, J. Kopáček, J. Safanda, S. A. Norton

► To cite this version:

J. Veselý, V. Majer, J. Kopáček, J. Safanda, S. A. Norton. Increasing silicon concentrations in Bohemian Forest lakes. *Hydrology and Earth System Sciences Discussions*, 2005, 9 (6), pp.699-706. hal-00304886

HAL Id: hal-00304886

<https://hal.science/hal-00304886>

Submitted on 31 Dec 2005

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Increasing silicon concentrations in Bohemian Forest lakes

J. Veselý¹, V. Majer¹, J. Kopáček², J. Safanda³ and S.A.Norton⁴

¹Department of Geochemistry, Czech Geological Survey, Geologická 6, 152 00 Prague 5, Czech Republic

²Hydrobiological Institute AS CR and Faculty of Biological Sciences USB, Na Sádkách 7, 370 05 České Budejovice, Czech Republic

³Geophysical Institute AS CR, Bocní II, 14 000 Praha-Sporilov, Czech Republic

⁴Department of Earth Sciences, Bryand Global Sciences Center, University of Maine, Orono, Maine, 04469- 5790, USA

E-mail for corresponding author: vesely@cgu.cz

Abstract

Long-term trends of dissolved silicon (Si) concentrations in five glacial lakes in the Bohemian Forest, Czech Republic, recovering from acidification show higher mobility of Si from the soil to surface waters despite lower atmospheric deposition of acids. Si increased by 0.95 to 1.95 $\mu\text{mol yr}^{-1}$ (36 to 51%) from 1986–2004 and with increasing pH. A change in soil solution conditions because of a sharp decrease in acidic deposition has led to marked decline in Al mobility and to considerable decreases in dissolved Al, especially Al^{3+} . The increase in Si may be related to: (1) unblocking of the inhibitory effect of dissolved Al on weathering of aluminosilicates, (2) biogenic opal (phytoliths) dissolving faster, and/or (3) lower Si precipitation as secondary aluminosilicates in soil. The change in Al speciation on the dissolution rate of biogenic silica is critical. A lack of change in Si at sites outside central Europe may be explained by small or no decline in mobility of dissolved Al. The effect of a long-term increase in temperature was probably minor.

Keywords: acidification, aluminium, Bohemian Forest, lake, phytoliths, silicon, silica, silicic acid, temperature

Introduction

Changes in silicon (Si) concentrations and fluxes of Si from terrestrial systems may reflect changes in chemical weathering. On a geological time scale of millions of years, changes in weathering rates affect the CO_2 concentration in the atmosphere through weathering of silicate minerals and transfer of CO_2 from the atmosphere to the lithosphere, primarily as CaCO_3 (Berner, 1994; Conley, 2002). Silicic acid may moderate Al toxicity in acidic soil (Lumsdon and Farmer, 1995; Hodson and Sangster, 1999; Exley *et al.*, 2002) and the biological availability of phosphorus in the presence of aluminium (Exley *et al.*, 1993; Kopáček *et al.*, 2000; Krivtsov *et al.*, 2000). Si may inhibit Al-induced reduction of bioavailable phosphorus by binding Al preferentially. Short-term variability of Si concentrations in streams relates to hydrology (Johnson *et al.*, 1969), season (Norton *et al.*, 1999; Gérard *et al.*, 2002; Soulsby *et al.*, 2001) and diatom utilisation (Clarke, 2003).

The chemical weathering of silicate minerals is the primary source of Si in the environment (Oliva *et al.*, 2003; White

and Blum, 1995) but biogenic silica (BSi = phytoliths + diatoms fossils) may be the principal immediate source of Si in soil solution (Farmer *et al.*, 2005). Si is not conservative during weathering. Vegetation causes higher soil acidity through the production of organic acids and elevated carbonic acid (Marchetto *et al.*, 1995), both of which accelerate chemical weathering. Plants play a major role in the recycling of soluble silica. Vegetation produces phytoliths, which return Si to soil with litter (Bartoli and Wilding, 1980; Conley, 2002; Farmer, 2005). Soils may have several percent of phytoliths. Wood species produce a high proportion of phytoliths containing Al (Cartelli *et al.*, 2002). Dissolution rates of phytoliths may vary by 1–2 orders of magnitude, depending on coatings and Al concentration (Iler, 1973; Van Bennekom *et al.*, 1989). Lake sediment contains up to tens of percent of diatoms and sponge spicules (Clarke, 2003). Interstitial water of lake sediment is enriched with dissolved Si that diffuses back into water (House *et al.*, 2000; Rickert *et al.*, 2002), increasing Si in the water column in the lake. In streams and lakes, dissolved Si

originates considerably from the dissolution of biogenic silica (Farmer *et al.*, 2005). Determination of Ge/Si ratios (Derry *et al.*, 2005) enables determination of the relative contribution of two main sources of Si (BSi and non-biogenic (soil minerals)) to Si cycling.

Here, 18-year trends in Si concentrations in five lakes and their principal inlets in the Bohemian Forest, Czech Republic, have been examined. This central European area has been recovering rapidly from atmospheric acidification (Veselý *et al.*, 1998a; Kopáček *et al.*, 2001) with a subsequent decrease in dissolved Al in streams and lakes (Veselý *et al.*, 1998b) and is experiencing a significant increase in average annual air temperature (Kettle *et al.*, 2003; Veselý *et al.*, 2003). The effects of increased temperature and decreased Al concentrations on the long-term increases of Si concentrations have also been evaluated.

Sites and Methods

Small lakes of glacial origin (Plešné, Certovo, Cerné, and Prášilské) are situated in the Bohemian Forest of the south-western Czech Republic between 13°11' and 13°52' E, and 48°47' and 49°11' N at elevations of 1008 to 1090 m a.s.l. Their water residence times are less than 20 months. Bedrock is granite in the Plešné Lake catchment and predominantly schist in the catchments of the other lakes (Veselý, 1994). Soils are acidic (pH_{CaCl2} of 2.5–4.5) and shallow (< 0.2 m deep) leptosol or < 0.5 m deep spodo-dystric cambisol and podzol. Base saturation is low (9–15 %) (Kopáček *et al.*, 2002). All but the Prášilské catchment are forested with 90 to 150-year old Norway spruce. During the present monitoring, the Prášilské catchment was ~50 % deforested by gales and bark beetle infestation.

Lake water samples were collected each year from the epilimnion of each lake and a principal inlet to the lake near the end of July and in the second half of October. Four to six water samples were collected during each sampling. Numerical average concentrations for each sampling were used for this analysis. During thermal stratification in July, samples were also collected from four to six depths in each lake between the surface and bottom at the deepest points in the lake and volume-weighted mean lake concentrations were calculated using known bathymetry. Seventeen inlets to Certovo, Plešné and Cerné lakes were sampled approximately monthly from 1997 to 2003.

Analytical methods are described in Veselý *et al.* (1998a) and Kopáček *et al.* (2000) and were identical throughout the study. Total Si and Al in lakes were determined by ICP-OES, and dissolved Si by the molybdate-blue technique in filtered (0.45 µm) lake samples. The difference between total Si and *in situ* dialyzable Si (in true solution) in lake samples

was ≤ 10%. Labile (ionic) aluminium (Al_i) was determined according to Driscoll (1984) and Dougan and Wilson (1974).

Data on air temperature and precipitation at Churánov station (at 1118 m a.s.l. among the lakes in the Bohemian Forest) were from the Czech Hydrometeorological Institute. Bulk precipitation during the 12-month period preceding lake sampling ranged from 846 mm (1991/92) to 1661 mm (2001/02) at Churánov site with no significant trend over the study period. Changes in ground temperature, caused by increasing air temperature, were calculated; air temperature is a crude but reasonable surrogate for soil temperature (Velbel, 1993). The mean air temperatures of the individual hydrological years observed since 1961 at Churánov were used as a forcing function at the ground surface. Negative values of monthly air temperature averages were substituted by 0 °C for calculation due to snow insulation of bedrock in winter. Subsurface temperatures at several depths and times were calculated according to Lewis (1992) using values of thermal conductivity of $1.0 \times 10^{-6} \text{ m}^{-2} \text{ s}^{-1}$ and $1.3 \times 10^{-6} \text{ m}^{-2} \text{ s}^{-1}$ for mica schist and granites, respectively.

Results

LONG-TERM TRENDS IN SI CONCENTRATIONS

Mean concentrations of Si in the lakes ranged from 51 to 99 µmol L⁻¹. The highest was Plešné Lake, situated on coarse-grained granite. Increasing Si concentrations occurred in all the lakes (Figs. 1 and 2) and in many inlets. The rate of Si increase in lakes ranges from 0.95 to 1.95 µmol L⁻¹ yr⁻¹ between 1986 and 2004, a relative increase of 36 to 51% in 18 years. The Si increase in lakes and tributaries was more pronounced between 1994 and 2001 (see Cerné in Fig. 1). Concentrations of Si in lakes and residuals of Si, ΔSi, from a linear increase with time, do not relate directly ($p < 0.05$) to average air temperature or precipitation volume in the year preceding sampling. Concentrations of Si in the principal inlets were generally higher and increased from 2.14 to 3.48 µmol L⁻¹ yr⁻¹, i.e. faster than in lake water (Fig. 1). Because concentrations of Si in precipitation are < 3.3 µmol Si L⁻¹, the source of the Si increase must be terrestrial.

Concentrations of Si were regularly lower in weakly acidified, shallow Laka Lake in summer (Fig. 2) when surface warming supports Si and NO₃ depletion by phytoplankton and uptake of Si from soil solutions by vegetation (Farmer *et al.*, 2005; Soulsby *et al.*, 2001). This seasonal variation occurs only in this lake and is superimposed on the long-term increase of Si concentrations observed for both the July and October sampling (Fig. 2).

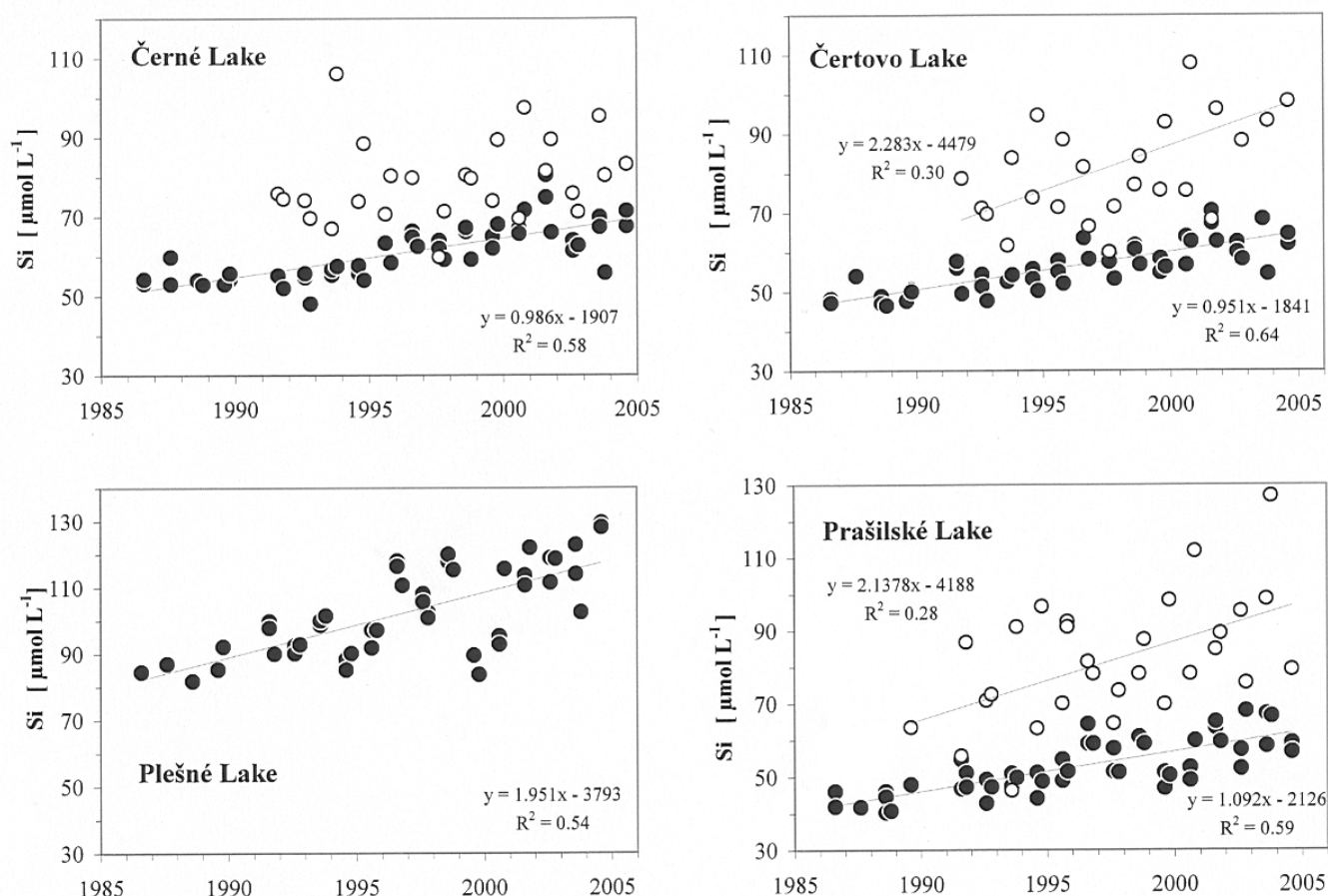


Fig. 1. Concentrations of Si in the Bohemian Forest lakes and main inlets from 1986–2004. ● – the average concentrations of Si for lakes in July and October; ○ – Si in main inlet; dotted lines = regression; an inlet to Černé Lake was only main inlet to lakes without a significant ($p < 0.05$) increase in Si concentration.

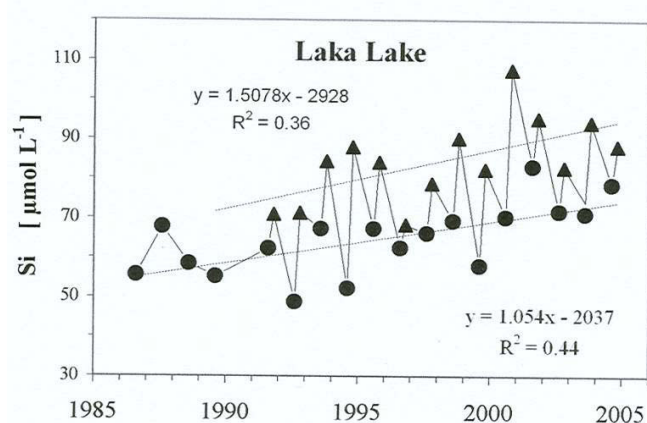


Fig. 2. Concentrations of Si in Laka Lake from 1986–2004. The average concentrations of Si are presented separately for July (●) and October (▲); the autumn concentrations were regularly higher in the lake suggesting seasonal variability in Si concentration in this weakly acidic and shallow lake. However, Si concentrations have increased both in summer and autumn.

Concentrations of total Al (Al_T) were relatively low ($< 10 \mu\text{mol L}^{-1}$) and Al was mostly bound to dissolved organic matter in Laka Lake due to a higher mean pH ($\text{pH} \sim 5.7$). In the four more acidified lakes, Si and Al_T were negatively related (Fig. 3). In these lakes, Al concentrations were related to concentrations of strong acid anions (SAA = sulphate + nitrate + chloride), i.e. to acidic atmospheric deposition (Veselý *et al.*, 2003; Veselý *et al.*, 1998b). The Si concentrations were negatively related to SAA.

The linear Si–Al relationship (Fig. 3) probably represents a connection between Si concentration and atmospheric deposition of acids and Al may be an intermediate (Van Bennekom *et al.*, 1989). The logarithm of Si concentration increased with the pH in the four strongly acidified lakes (e.g. Prašilské Lake, Fig. 4a). The relative increase in Si, $\Delta\text{Si} / \text{Si}$, defined as the ratio between the change in Si concentration and mean Si concentration over the study period, ranged between 0.016 and 0.023 yr^{-1} . $\Delta\text{Si} / \text{Si}$ probably increases with mean pH in weakly acid lake water

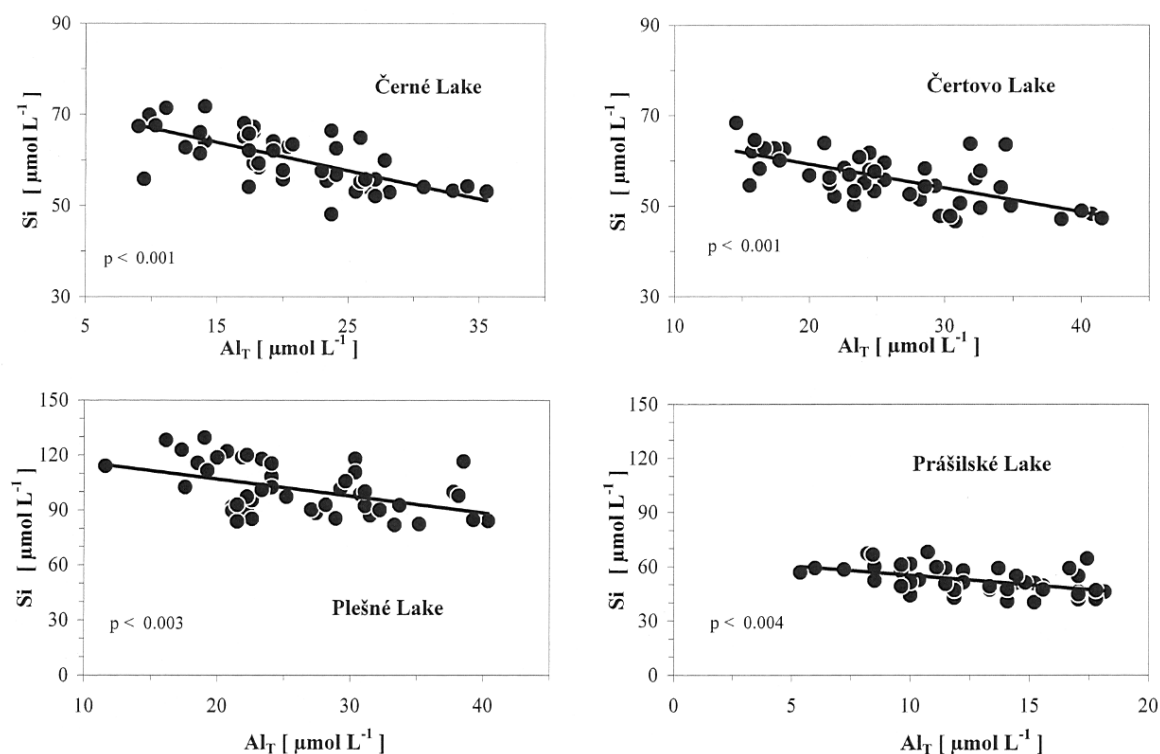


Fig. 3. Relationships between Si and Al_T in formerly highly acidified lakes from 1986–2004. Strong inter-relationship between Si and Al concentrations suggests they are regularly related.

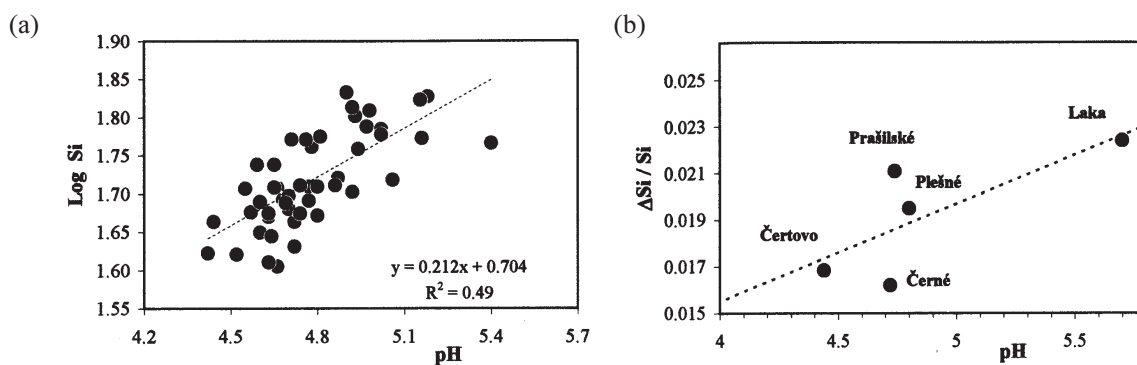


Fig. 4 (a) Relationship between Log Si and pH in Prášílské Lake from 1986–2004. Concentrations of Log Si have increased with pH suggesting that the process behind the Si increase in the lakes is dependent on the acid-base status in the catchment. (b) Relationship between relative increase of Si ($\Delta Si / Si$) and pH.

(Fig. 4b). The processes controlling change of Si in lake water are pH-dependent (Fig. 4). However, the present results, surprisingly, show higher mobility of Si with increasing pH and in spite of lower deposition of acids.

Short-term variability of Si in streams

Daily and seasonal fluctuations in stream chemistry are dependent on many processes, especially mixing of base- and storm-flow. In most of the inlets to the lakes,

concentrations of Si decreased exponentially with increasing discharge (Q) (Fig. 5a). Decreases in solute concentrations with runoff are commonly attributed to dilution of base flow chemistry by storm- or melt-water. To separate short-term chemical effects from hydrological control in tributaries, residuals of Si were calculated from a linear regression of Si against log Q. Residuals, ΔSi , for nine of the 17 streams sampled from 1997 to 2003 were negatively related ($p < 0.05$) to stream water temperature (Fig. 5b). At higher stream water temperatures, Si concentrations tended to be below

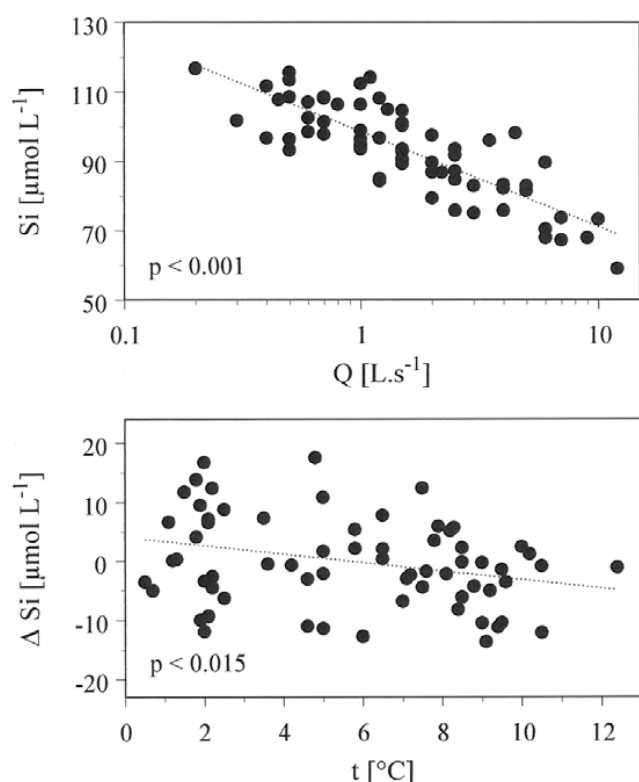


Fig. 5 (a) Relationship between Si and log discharge (Q) from lake tributaries. Concentrations of Si decreased exponentially with discharge in most tributaries. (b) Residuals of Si, (ΔSi), from linear regression of Si with log Q were generally more negative at higher temperature. To separate temperature from hydrological effects, residuals of Si, (ΔSi), from a linear regression of Si against log Q were calculated at higher stream water temperatures, Si concentrations tend to be below the regression line in most of streams. The likely cause is increased plant uptake of Si from soil solution during the growing season.

the Si/Log Q regression line in most of the streams. This suggests uptake of Si by vegetation at higher seasonal temperatures.

Discussion

Acidification of the lakes peaked in the mid-1980s (Vrba *et al.*, 2003; Kopáček *et al.*, 2001; Veselý *et al.*, 1998a). From 1986 to 2004, Si has increased, Na has remained relatively constant and concentrations of all other major solutes have decreased. Strong decrease of the SAA in water was compensated mostly by reduction of inorganic (labile) Al (Veselý *et al.*, 1998b; Kopáček *et al.*, 2000). The decline in inorganic Al was enhanced by climate warming (Veselý *et al.*, 2003).

The concentrations of Si in the five lakes increased by 36 to 51% between the summers of 1986 and 2004. Repeated regional surveys of freshwaters in the Czech Republic and

small catchment monitoring (Hruška *et al.*, 2002) showed that the increase in Si concentration is a general phenomenon for mountainous-forested areas in that period. Concentrations of Si have increased also in lakes of the Alps (Sommaruga-Wögrath *et al.*, 1997; Rogora *et al.*, 2003), and in northern-Italian rivers (Mossello *et al.*, 2000). In contrast, volume-weighted concentrations of Si in the Hubbard Brook Experimental Forest stream water show no long-term trend over the 1965–1987 period (Driscoll *et al.*, 1989). Si was unchanged in a pair of acidifying streams at the Bear Brook Watershed in Maine for the period 1987–2003 (Norton *et al.*, 1999). Therefore, there are regional differences in long-term trends in Si concentrations. Two hypotheses have been explored to explain the long-term increase observed in Si concentrations in the Czech Republic:

1. *Effect of temperature (climate warming).* The increase of Si in lakes of the Alps was accompanied by an increase in base cations that was explained by an increase in the rate of weathering induced by climate warming (Sommaruga-Wögrath *et al.*, 1997). The present study is in an area of warming (Weber *et al.*, 1997; Schär *et al.*, 2004) and a negative effect of temperature on Al concentrations in the same lakes has been observed. While the solubility of BSi and weathering rate increase with temperature, the solubility of the secondary aluminosilicates decreases. Consequently, the possible effects of increasing temperature on Si concentrations have been evaluated.

Average weathering rates of minerals depend on temperature according to the Arrhenius law (White and Blum, 1995):

$$K_w(T) = K_w^\circ \exp(-E_a/RT) \quad (1)$$

where K_w is the rate constant ($\text{mol ha}^{-1} \text{ yr}^{-1}$) at temperature T (K degrees), K_w° is its value at a given reference temperature, E_a is apparent activation energy of the reaction and R is the gas constant ($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$). Average air temperature in the year preceding water sampling ranged from 3.28 to 5.75 °C in the Bohemian Forest and increased irregularly during the 18-years of observation (Kettle *et al.*, 2003; Veselý *et al.*, 2003). Long-term warming proceeds slowly from soil into bedrock where temperature change lags behind air temperature change substantially. Calculated theoretical change in subsurface (bedrock) temperature with depth over the period 2004 to 1986 was about 0.7, 0.45, and ~ 0.35 °C at depths of 0, 10 and 20 m respectively. From Eqn.1 for $E_a = 69 \text{ kJ mol}^{-1}$ (White and Blum, 1995) a warming theoretically increases the weathering rate by about 8, 5, and 4% at depths of 0, 10 and 20 m, respectively.

Concentrations of Si in the lakes have increased substantially more.

Dissolution of amorphous (biogenic) silica also increases with temperature. The change in equilibrium solubility of BSi caused by long-term temperature change over the period studied can be calculated from

$$\ln (K_{T_1}/K_{T_0}) = -\Delta H_r^\circ / R [1/T_1 - 1/T_0] \quad (2)$$

where ΔH_r° is the standard heat of dissolution for the reaction, R is the gas constant, T_1 and T_0 are temperatures in K degrees at the beginning and end of the study. The effect of a temperature increase of $\sim 0.7^\circ\text{C}$ on the solubility of amorphous silica and phytoliths suggests an increase in Si of only about 2% for standard heats of dissolution, $\Delta H_r^\circ = 15$ (amorphous silica) and 22 (phytoliths) kJ mol^{-1} (Farmer *et al.*, 2005; Gustafsson *et al.*, 2001). Increased temperature also enhances evapotranspiration and vegetative cycling of Si. More frequent soil drying (Simonsson *et al.*, 1999) and less frequent soil freezing (Dietzel, 2005) may also contribute to an increase in Si in freshwater. Nevertheless, combined temperature effects cannot explain the relative increase in Si observed in the lakes. Lastly, the dissolution of forest phytoliths is independent of pH at values below 6 (Bartoli and Wilding, 1980) but the process behind the increase in Si in lakes is pH-related.

2. Decrease in Al mobility. Atmospheric acidic deposition has decreased sharply (Kopáček and Veselý, 2005), the pH of lake waters has increased (Fig. 4a) and, consequently, the mobility of Al decreased substantially. Si is negatively related to Al (Fig. 3). The relative change in Si, ($\Delta\text{Si} / \text{Si}$), may increase with mean pH of lake water in the range 4.4 to 5.7 as well as log Si concentrations with increasing pH (Fig. 4). The process behind the long-term increase in Si is more obvious at higher pH in weakly acidic environments where dissolved Al concentrations become especially low. Concentrations of Al_T have decreased 60 to 75% from initial values of 41 to 18 $\mu\text{mol L}^{-1}$ and concentrations (activity) of Al^{3+} even more. Three alternative hypotheses are proposed:

- (a) less Si may be precipitated in soil as secondary aluminosilicates (Doucet *et al.*, 2001; Exley *et al.*, 2002), because of lower amounts of Al dissolved in the soil solution. Silica that previously was precipitated as secondary aluminosilicates may remain free, increasing Si in soil solutions, streams and lake water;
- (b) lower Al mobility means lower incorporation of Al into and adsorption onto BSi (phytoliths and diatoms). Aluminium on these phases dramatically slows down BSi dissolution (Iler, 1973; Bartoli and Wilding, 1980;

Van Bennekom *et al.*, 1989; Dixit *et al.*, 2001; Rickert *et al.*, 2002). Al-free BSi dissolution kinetics may be much faster;

- (c) lower dissolved Al means less restricted weathering (Chou and Wollast, 1985; Gérard *et al.*, 1998). Above certain Al concentrations, rates of dissolution of aluminosilicates at constant pH exhibit a negative dependence on dissolved Al (e.g. Oelkers *et al.*, 1994). However, primary weathering should be related to pH negatively, in that Si should increase with decreasing pH; this is not what is observed. Precipitation of most secondary aluminosilicates increases with temperature. Therefore, from all the above options, the kinetic effect of Al speciation on the dissolution rate of BSi, the solubility of which is independent of pH below 6 (Bartoli and Wilding, 1980) is preferred. The increase in Si is dependent on pH due to an acid-base limitation of Al solubility and migration in a weakly acidic environment.

Conclusion

Silica concentrations in five Czech lakes have increased despite lower acid deposition. This behaviour of Si is paradoxical because weathering (the primary source of Si) should accelerate in more acidic environments. Yet, it seems that a sharp decrease in soil Al mobility and dissolved Al increases the rate of biogenic silica dissolution. Concentrations of ionic Al decreased, primarily because of a reduction in atmospheric deposition of acids coupled with increased soil water pH and secondarily because of temperature increases. If correct, the effect will decline as Al^{3+} concentration becomes so low that the dissolution rate of BSi becomes independent of free Al concentration as is the case in many parts of the world. Climate warming adds to the decrease in Al. The change in Si concentration in lakes was kinetically rather than thermodynamically induced.

Acknowledgements

This research has been supported in part by the Grant Agency of the Czech Republic (206/03/1583), the Environment Project of European Commission EUROLIMPACS (GOCE-CT-2003-505540) and the US National Science Foundation grants DEB045348 and DEB--210257 (Norton).

References

- Bartoli, F. and Wilding, L.P., 1980. Dissolution of biogenic opal as a function of its physical and chemical properties. *Soil Sci. Soc. Amer. J.*, **44**, 873–878.

- Berner, R.A., 1994. GEOCARB II: A revised model of atmospheric CO₂ over Phanerozoic time. *Amer. J. Sci.*, **294**, 56–91.
- Cartelli, A.L., Madella, M., Theurillat, J.P. and Ammann, B., 2002. Aluminum in opal silica reticulate of phytoliths: A new tool in palaeocological studies. *Amer. J. Bot.*, **89**, 346–351.
- Clarke, J., 2003. The occurrence and significance of biogenic opal in the regolith. *Earth-Sci. Rev.*, **60**, 175–194.
- Conley, D.J., 2002. Terrestrial ecosystems and the global biogeochemical silica cycle. *Global. Biogeochem. Cycle*, **16**, Art. No 1121, Dec. 6, 2002.
- Chou, L. and Wollast, R., 1985. Steady-state kinetics and dissolution mechanisms of albite. *Amer. J. Sci.*, **285**, 963–993.
- Derry, L.A., Kurtz, A.C., Ziegler, K. and Chadwick, O.A., 2005. Biological control of terrestrial silica cycling and export fluxes to watersheds. *Nature*, **433**, 728–731.
- Dietzel, M., 2005. Impact of cycling freezing on precipitation of silica in Me-SiO₂-H₂O systems and geochemical implications for cryosoils and sediments. *Chem. Geol.*, **216**, 76–88.
- Dixit, S., Van Cappellen, P. and Van Bennekom, A.J., 2001. Processes controlling solubility of biogenic silica and pore water build-up of silicic acid in marine sediments. *Mar. Chem.*, **73**, 333–352.
- Doucet, F.J., Schneider, C., Bones, S.J., Kretchmer, A., Moss, I., Tekely, P. and Exley, C., 2001. The formation of hydroxyaluminosilicates of geochemical and biological significance. *Geochim. Cosmochim. Acta*, **65**, 2461–2467.
- Dougan, W.K. and Wilson, A.L., 1974. The absorptometric determination of aluminium in water. A comparison of some chromogenic reagents and the development of an improved method. *Analyst*, **99**, 413–430.
- Driscoll, C.T., 1984. A procedure for the fractionation of aqueous aluminum in dilute acidic waters. *Anal. Chem.*, **16**, 267–284.
- Driscoll, C.T., Likens, G.E., Hedin, L.O., Eaton, J.S. and Bormann, F.H., 1989. Changes in the chemistry of surface waters. *Environ. Sci. Technol.*, **23**, 137–143.
- Exley, C., Schneider, C. and Doucet, F.J., 2002. The reaction of aluminium with silicic acid in acidic solution: an important mechanism in controlling the biological availability of aluminium. *Coord. Chem. Rev.*, **228**, 127–135.
- Exley, C., Tollervey, A., Gray, G., Roberts, S. and Birchall, J.D., 1993. Silicon, aluminum and the biological availability of phosphorus in algae. *Proc. Roy. Soc. London., B.*, **253**, 93–99.
- Farmer, V.C., 2005. Forest vegetation does recycle substantial amounts of silicon from and back to the soil solution with phytoliths as an intermediate phase, contrary to recent reports. *Eur. J. Soil. Sci.*, **56**, 271–272.
- Farmer, V.C., Delbos, E. and Miller, J.D., 2005. The role of phytolith formation and dissolution in controlling concentrations of silica in soil solutions and streams. *Geoderma*, **127**, 71–79.
- Gérard, F., Francois, M. and Ranger, J., 2002. Processes controlling silica concentration in leaching and capillary soil solutions of an acidic brown forest soil (Rhône, France). *Geoderma*, **107**, 197–226.
- Gérard, F., Fritz, B., Clement, A. and Crovisier, J.L., 1998. General implications of aluminium speciation-dependent kinetic dissolution rate law in water-rock modelling. *Chem. Geol.*, **151**, 247–258.
- Gustafsson, J.P., Berggren D., Simonsson, M., Zysset, M. and Mulder, J., 2001. Aluminium solubility mechanisms in moderately acid Bs horizons of podzolized soils. *Eur. J. Soil. Sci.*, **52**, 655–665.
- Hodson, M.J. and Sangster, A.G., 1999. Aluminium/silicon interactions in conifers. *J. Inorg. Biochem.*, **76**, 89–98.
- House, W.A., Denison, F.H., Warwick, M.S. and Zhmud, B.V., 2000. Dissolution of silica and the development of concentration profiles in freshwater sediments. *Appl. Geochem.*, **15**, 425–438.
- Hruška, J., Moldan, F. and Krám, P., 2002. Recovery from acidification in central Europe – observed and predicted changes of soil and streamwater chemistry in the Lysina catchment, Czech Republic. *Environ. Pollut.*, **120**, 261–264.
- Iler, R.K., 1973. Effect of absorbed alumina on the solubility of amorphous silica in water. *J. Colloid Interface Sci.*, **43**, 399–408.
- Johnson, N.M., Likens, G.E., Bormann, F.H., Fisher, D.W. and Pierce, R.S., 1969. A working model for the variation in stream waters chemistry at the Hubbard Brook Experimental Forest, New Hampshire. *Water Resour. Res.*, **5**, 1353–1363.
- Kettle, H., Kopáček, J. and Hejzlar, J., 2003. Modelling air temperature at Certovo Lake back to 1781. *Silva Gabreta*, **9**, 15–32.
- Kopáček, J. and Veselý, J., (2005). Sulphur and nitrogen emissions in the Czech Republic and Slovakia between 1850 and 2000. *Atmosph. Environ.*, **39**, 2179–2188.
- Kopáček, J., Hejzlar, J., Borovec, J., Porcal, P. and Kotorová, I., 2000. Phosphorus inactivation by aluminum in the water column and sediments: Lowering of in-lake phosphorus availability in an acidified watershed-lake ecosystem. *Limnol. Oceanogr.*, **45**, 212–225.
- Kopáček, J., Veselý, J. and Stuchlík, E., 2001. Sulphur and nitrogen fluxes and budgets in the Bohemian Forest and Tatra Mountains during the Industrial Revolution (1850–2000). *Hydrol. Earth Syst. Sci.*, **5**, 391–405.
- Kopáček, J., Kana, J., Santrucková, H., Porcal, P., Hejzlar, J., Píček, T. and Veselý, J., 2002. Physical, chemical, and biochemical characteristics of soils in watersheds of the Bohemian Forest lakes: II. ertovo and erné Lake. *Silva Gabreta*, **8**, 67–94.
- Krivtsov, V., Bellinger, E., Sigee, D. and Corliss, J., 2000. Interrelations between Si and P biogeochemical cycles – a new approach to the solution of the eutrophication problem. *Hydrol. Process.*, **14**, 283–295.
- Lewis, T., (Ed.), 1992. Climatic change inferred from underground temperatures. *Global. Planet. Change*, **98**, 71–281 (Special Issue).
- Lumsdon, D.G. and Farmer, V.C., 1995. Solubility characteristics of proto-imogolite sols – how silicic acid de-toxify aluminum solutions. *Eur. J. Soil. Sci.*, **46**, 179–186.
- Marchetto, A., Mosello, R., Psenner, R., Bendetta, G., Boggero, A., Tait, D. and Tartari, G.A., 1995. Factors affecting water chemistry of alpine lakes. *Aquat. Sci.*, **57**, 81–89.
- Mosello, R., Marchetto, A., Brizzio, M.C., Rogora, M. and Tartari, G.A., 2000. Results from the Italian participation in the International Co-operative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes. *J. Limnol.*, **59**, 47–54.
- Norton, S.A., Kahl, J., Fernandez, I., Haines, T., Rustad, L., Nodvin, S., Scofield, J., Strickland, T., Erickson, H., Wigington, P. (Jr.) and Lee, J., 1999. The Bear Brook Watershed, Maine (BBWM), USA. *Environ. Monit. Assess.*, **55**, 7–51.
- Oelkers, E.H., Schott J. and Devidal, J.L., 1994. The effect of aluminium, pH, and chemical affinity on the rates of aluminosilicate dissolution reactions. *Geochim. Cosmochim. Acta*, **58**, 2011–2024.
- Oliva, P., Viers, J. and Dupré, B., 2003. Chemical weathering in granitic environments. *Chem. Geol.*, **202**, 225–256.
- Rickert, D., Schlüter, M. and Wallmann, K., 2002. Dissolution kinetics of biogenic silica from the water column to the sediments. *Geochim. Cosmochim. Acta*, **66**, 439–455.
- Rogora, M., Mosello, R. and Arisci, S., 2003. The effect of climate warming on the hydrochemistry of alpine lakes. *Water Air Soil Pollut.*, **148**, 347–361.

- Schär, C., Vidale, P.L., Lüthi, D., Frei, C., Häberli, C., Liniger, M.A. and Appenzeller, C., 2004. The role of increasing temperature variability in European summer heatwaves. *Nature*, **427**, 332–336.
- Simonsson, M., Bergren, D. and Gustafsson, J.P., 1999. Solubility of aluminum and silica in spodic horizons as affected by drying and freezing. *Soil Sci. Soc. Amer. J.*, **63**, 1116–1123.
- Sommaruga-Wögrath, S., Koinig, K.A., Schmidt, R., Sommaruga, R., Tessadri, R. and Psenner, R., 1997. Temperature effects on the acidity of remote alpine lakes. *Nature*, **387**, 64–67.
- Soulsby, C., Malcolm, R., Gibbins, C. and Dilks, C., 2001. Seasonality, water quality trends and biological resources in four streams in the Cairngorm Mountains, Scotland. *Hydrol. Earth Syst. Sci.*, **5**, 433–450.
- Van Bennekom, A.J., Jansen, J.H.F., Van der Gaast, S.J., Van Iperen, J.M. and Pieters, J., 1989. Aluminium-rich opal: An intermediate in the preservation of biogenic silica in the Zaire (Congo) deep-sea fan. *Deep-Sea Res.*, **36**, 173–190.
- Velbel, M.A., 1993. Temperature dependence of silicate weathering in nature. *Geology*, **21**, 1059–1062.
- Veselý, J., 1994. Investigation of the nature of the Šumava lakes: a review. *Cas. Národ. Muzea, Praha, R. Přírod.*, **163**, 103–120.
- Veselý, J., Hruška, J. and Norton, S.A., 1998b. Trends in the chemistry of acidified Bohemian lakes from 1984 to 1995: II. Trace elements and aluminum. *Water Air Soil Pollut.*, **108**, 425–443.
- Veselý, J., Hruška, J. and Norton, S.A., 2002. Heterogenous response of central European streams to decreased acidic atmospheric deposition. *Environ. Pollut.*, **120**, 275–281.
- Veselý, J., Hruška, J., Norton, S.A. and Johnson, C.E., 1998a. Trends in the chemistry of acidified Bohemian lakes from 1984 to 1995: I. Major solutes. *Water Air Soil Pollut.*, **108**, 107–127.
- Veselý, J., Majer, V., Kopáček, J. and Norton, S.A., 2003. Increasing temperature decreases aluminum concentrations in central European lakes recovering from acidification. *Limnol. Oceanogr.*, **48**, 2346–2354.
- Vrba, J., Kopáček, J., Fott, J., Kohout, L., Nedbalová, L., Pražáková, M., Soldán, T. and Schaumburg, J., 2003. Long-term studies (1871–2000) on acidification and recovery of lakes in the Bohemian Forest (central Europe). *Sci. Total Environ.*, **310**, 73–85.
- Weber, R.O., Talkner, P., Auer, I., Böhm, R., Gajic-Capka, M., Zaninovic, K., Brázdil, R. and Faško, P., 1997. 20th-century changes of temperature in the mountain regions of Central Europe. *Climatic Change*, **36**, 327–344.
- White, A.F. and Blum, A.E., 1995. Effects of climate on chemical weathering in watersheds. *Geochim. Cosmochim. Acta*, **59**, 1729–1747.